STUDIES ON ENERGETIC COMPOUNDS
Part 40. Kinetics of thermal decomposition of some bis(propylenediamine)metal perchlorate complexes

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Bis(propylenediamine)metal perchlorate (BPMP) complexes like $[M(pn)_2](ClO_4)_2$ (where *M*=Cr, Mn, Ni, Cu, Zn and *pn*=propylenediamine) have been prepared and characterized by gravimetric methods, infrared and elemental analysis. Thermal properties have been studied using simultaneous thermogravimetry-differential thermal analysis in atmospheres of nitrogen and air to examine the effect of atmospheric change on thermal decomposition of these complexes. Changing of the atmosphere does not cause any measurable changes in the decomposition of complexes. However, as indicated by thermoanalytical techniques, the thermal stability of present complexes decreases in the order: $[Cr(pn)_2](ClO_4)_2 > [Mn(pn)_2](ClO_4)_2 > [Zn(pn)_2](ClO_4)_2 > [Ni(pn)_2](ClO_4)_2 > [Cu(pn)_2](ClO_4)_2$. Isothermal thermogravimetry, over the temperature range of decomposition has been done for all the complexes. An analysis of the kinetics of thermal decomposition was made using a model fitting procedure as well as an isoconversional method, independent of any model. The results of both kinetic approaches have been discussed critically. The explosion delay (D_E) was measured to investigate the trend of rapid thermal analysis.

Introduction

Energetic transition metal complexes are well-known explosives because of the presence of both oxidizing and reducing group in the same complex molecule. These complexes may find interesting applications in pyrotechnic composition. The substances used in the past in such composition are now avoided since they lead to environmental and health problems. Some alternative metal complexes have been synthesized to replace the conventional oxidizers like lead azide, potassium nitrate, etc., in view of their inherent drawbacks such as friction sensitivity, lesser stability to moisture and incompatibility with other materials used in ammunition. Nickel hydrazine nitrate [1] has been prepared and found insensitive to impact, friction or electrostatic charge but more sensitive to flame [2]. It is a suitable replacement for lead azide, as an intermediate charge in commercial detonators. Also, the reaction liquor, unlike lead azide, does not contain any useless ion and thus makes possible the repeated use of the liquor in continuous preparation of this primary explosive. N,N-bis(2,4,6-trinitrobenzoyl)lead hydrazine, synthesized from lead acetate and bis(2,4,6-trinitrobenzoyl)hydrazine with better heat resistance properties is found to be a good substitute for lead styphnate [3]. Cobalt perchlorate complex with diaminourea has been proved to be a quite good initiator for use as primary explosive [4]. Also, such complexes are potential

ballistic modifiers for composite solid propellants [5–7]. The ultra-fine metal oxide, which is the final product of thermal decomposition of these complexes, may find broad spectrum of applications. Thus, in view of exciting potential for various applications, the thermal studies were carried out in our laboratory. From the theoretical point of view, the interest is focused on the kinetics of thermal decomposition and from practical perspective; the study is aimed to explore the possibilities of using some energetic coordination compounds in pyrotechnic compositions.

Experimental

Materials

The following AR grade commercially available chemicals (obtained from the sources given in parentheses) were used as received without any further purification: Carbonates of copper, chromium, manganese (BDH), nickel, zinc (Thomas Baker), 70% perchloric acid, methanol (Ranbaxy), ethanol (Hayman), propylenediamine, silica gel, iodine (s.d. fine chemicals) and petroleum ether (Merck).

Preparation of complexes

Various BPMP complexes were prepared following a two-step procedure:

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Step I: in the first step, the metal carbonates (MCO_3) were treated with 70% perchloric acid ($HClO_4$) to produce the metal perchlorate, i.e. $M(ClO_4)_2$

$$MCO_3 + 2HClO_4 \rightarrow M(ClO_4)_2 + H_2O + CO_2$$

The perchlorates thus obtained were washed with petroleum ether, recrystallized from distilled water and dried in a desiccator over fused $CaCl_2$.

Step II: BPMP complexes were prepared by reacting an ethanolic solution of $M(ClO_4)_2$ from step I with propylenediamine following standard procedures [8–12]:

$$M(ClO_4)_2 + H_2N-(CH_2)_3-NH_2 \rightarrow [M(pn)_2](ClO_4)_2$$
$$(pn) \qquad\qquad (BPMP)$$

The precipitated complexes of different colours were separated from the mother liquor by decanting and washing with methanol. All these perchlorates were recrystallized from aqueous solution and dried over fused $CaCl_2$ in a desiccator.

Thermal decomposition studies

All the non-isothermal analyses were done at a heating rate of $10°C\ min^{-1}$. The simultaneous TG-DTA curves on the complexes (mass≈1–2 mg) were obtained on a Mettler Toledo Star system in an inert atmosphere (N_2 flowing at 100 mL min^{-1}). Non-isothermal TG curves were recorded on our indigenously fabricated TG apparatus [13] in static air (sample's mass≈10 mg, 100–200 mesh). Non-isothermal DTA curves were taken in flowing air (100 mL min^{-1}) using an instrument supplied by Universal Thermal Analysis Instruments, Mumbai (mass of sample≈10 mg). Isothermal TG on the complexes (mass≈10 mg) was done in static air using the indigenously fabricated TG [13] at appropriate temperatures of decomposition. The explosion delay (D_E) of a complex (mass≈10 mg) was measured using the tube furnace (TF) technique [14–16].

Results

Characterization

The purity of all these complexes was checked by thin layer chromatography (TLC) using a mixture of *n*-butanol, chloroform and glacial acetic acid in volume ratios of 2:1:1 as mobile phase (eluent). A yellow coloured spot was obtained in all the cases the R_f value of which is presented in Table 1. The metal content (%) was estimated gravimetrically by well established methods [17]. The percentage mass of other elements (C, H, N) was determined on Fission Instruments DP 200 series 2 systems. The complexes were further characterized by their infrared spectra (Impact 400) in

the form of their nujol mulls. The deduced molecular formulae of the complexes and their physical, elemental and spectral parameters are reported in Table 1.

TG-DTA

The simultaneous TG-DTA curves are presented in Fig. 1 and the corresponding data are listed in Table 2. All these BPMP complexes are decomposing in a single step. Mass loss occurs in the temperature range of 230–345°C, which corresponds to simultaneous losses of two molecules of ligands (*pn*) and counter anion (ClO_4^-) and approaching 60.5–81% of the initial mass. The mass of the residue corresponds to the formation of metal oxides. The rate of the reaction is fast and highly exothermic that is evident by accompanying sharp exothermic DTA peaks.

Non-isothermal TG and DTA in air

In order to detect the effect of changing the atmosphere on thermal decomposition, TG and DTA were used separately in static and flowing air. Non-isothermal TG and DTA curves are demonstrated in Figs 2 and 3, respectively. All of these complexes undergo decomposition in a single step and produce exothermicity in DTA.

Isothermal TG

Isothermal TG thermal curves were obtained over an optimal temperature of decomposition because of faster and slower decomposition at higher and lower temperatures, respectively. The desired temperature was maintained within ±1°C and mass loss readings were taken after suspending the sample into the furnace. The curves are shown in Fig. 4.

Mathematical treatment of isothermal TG data

Two methods were used to evaluate the kinetic parameters. A general equation for analyzing the kinetics of a thermally induced solid state reaction is,

$$d\alpha/dt = k(T)f(\alpha) \qquad (1)$$

where α is the degree of conversion, t represents time, T is the absolute temperature, $k(T)$ is the temperature-dependent rate constant and $f(\alpha)$ is a function called the reaction model. Various commonly used reaction models are known. It is assumed that the rate constant obeys the Arrhenius expression: $k(T) = A\exp(-E/RT)$, where A is the pre-exponential (Arrhenius) factor, E denotes the activation energy and R is the gas constant. The integral form of Eq. (1) is generally used in kinetic analysis giving
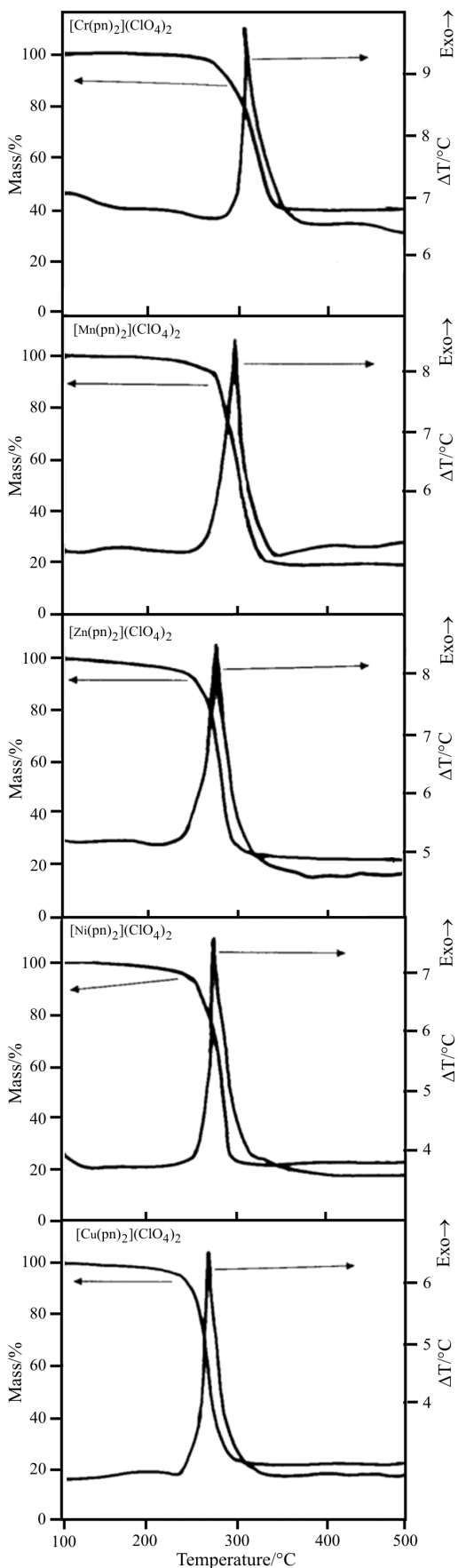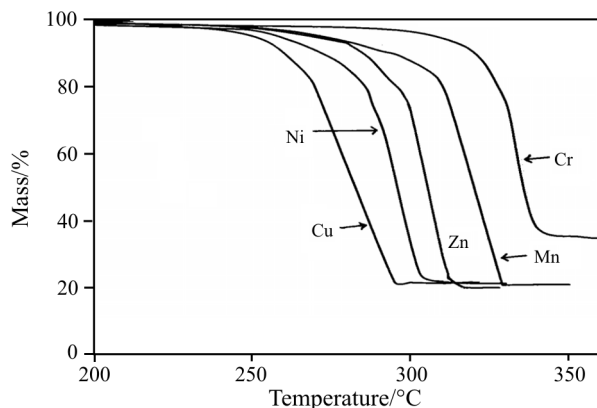
Fig. 1 TG-DTA curves of BPMP complexes in N$_2$

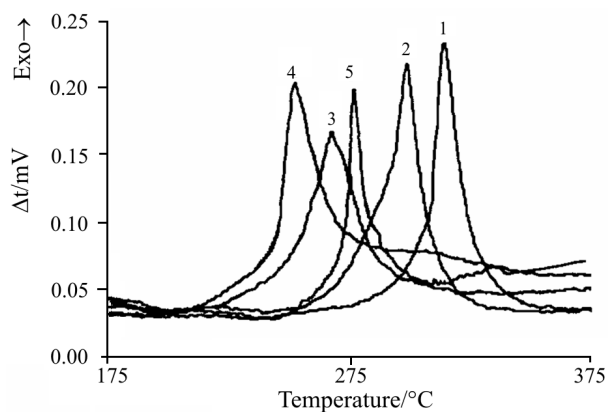Fig. 2 Non-isothermal TG curves of complexes recorded in air

Fig. 3 DTA curves obtained in air; 1 – [Cr(pn)$_2$](ClO$_4$)$_2$, 2 – [Mn(pn)$_2$](ClO$_4$)$_2$, 3 – [Ni(pn)$_2$](ClO$_4$)$_2$, 4 – [Cu(pn)$_2$](ClO$_4$)$_2$ and 5 – [Zn(pn)$_2$](ClO$_4$)$_2$

$$g(\alpha) \equiv \int_0^{\alpha} [f(\alpha)]^{-1} d\alpha = k(T)t \qquad (2)$$

at a constant temperature. Here the term $g(\alpha)$ represents an integral. Thus, substitution of a particular reaction model in Eq. (2) permits one to estimate the corresponding rate constant, obtained from the slope of a plot of $g(\alpha)$ *vs. t*. For every reaction model selected, the rate constants can be determined at several temperatures and the Arrhenius parameters were derived.

In the isoconversional method, it is assumed that the reaction model in Eq. (1) is independent of temperature, in which case

$$\ln\{g(\alpha)/t\} = \ln A - E_\alpha / RT \qquad (3)$$

where E_α (activation energy for a particular α) was determined from the slope of a plot of $-\ln t_\alpha$ *vs.* T^{-1}. Thus, the values of E_α for all the complexes were evaluated at various α_i. The dependencies of E_α on the extent of conversion (α) are shown in Fig. 5.

Table 1 Physical, elemental and spectral data profile of BPMP complexes

Complex	Colour	TLC*		Element/% observed (calculated)					IR**				
		Eluent	R_f	C	H	N	metal	vpn	$vM–N$	$vH_2N–CH_2$	$v(Cl=O)$	$v(Cl–O^-)$	ClO_4^-
[Cr(pn)$_2$] (ClO$_4$)$_2$	light green	2a:b:c	0.75	17.8 (18.0)	4.3 (5.0)	13.1 (14.0)	12.5 (13.0)	1089m	440s	1077m	585s	1115w	619s
[Mn(pn)$_2$](ClO$_4$)$_2$	brown	2a:b:c	0.79	17.1 (17.9)	4.2 (4.9)	13.5 (13.9)	12.9 (13.7)	1067m	438s	1065m	622s	1095w	620s
[Ni(pn)$_2$] (ClO$_4$)$_2$	violet	2a:b:c	0.71	17.0 (17.7)	4.3 (4.9)	13.2 (13.8)	13.8 (14.5)	1098m	442s	1102m	599s	1087w	618s
[Cu(pn)$_2$] (ClO$_4$)$_2$	dark blue	2a:b:c	0.68	16.6 (17.5)	4.0 (4.8)	12.9 (13.6)	14.8 (15.5)	1108m	436s	1090m	590s	1107w	619s
[Zn(pn)$_2$] (ClO$_4$)$_2$	white	2a:b:c	0.73	16.8 (17.5)	4.2 (4.9)	12.8 (13.6)	15.0 (15.8)	1099m	437s	1078m	618s	1118w	622s

*a=n-butanol, b=chloroform, c=gl. acetic acid, R_f=retention factor, locating reagent=iodine; **m=medium, s=sharp, w=wide
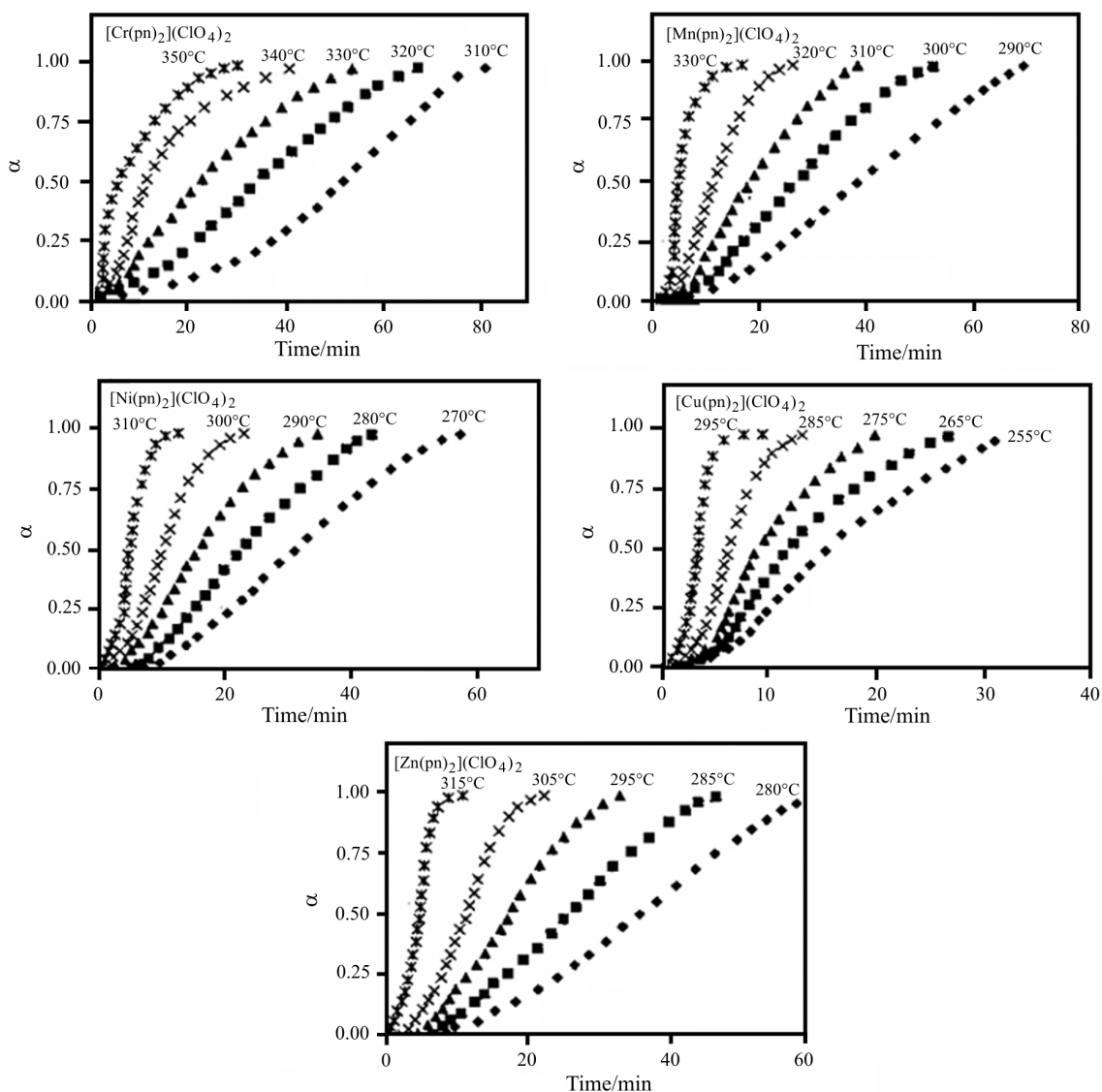
Fig. 4 Isothermal TG curves of BPMP complexes in air at the temperatures (°C) shown

Table 2 TG-DTA phenomenological data on BPMP complexes under N_2 atmosphere

Complex	TG				DTA peak temperature (exothermic)/°C
	T_i/°C	T_s/°C	T_f/°C	decomposition/%	
$[Cr(pn)_2](ClO_4)_2$	269	310	345	60.5	307
$[Mn(pn)_2](ClO_4)_2$	258	298	331	81.0	295
$[Ni(pn)_2](ClO_4)_2$	238	275	318	79.5	277
$[Cu(pn)_2](ClO_4)_2$	230	266	307	78.0	270
$[Zn(pn)_2](ClO_4)_2$	245	284	322	78.5	279

BPMP complexes under N_2 atmosphere; T_i=onset temperature, T_s=inflection temperature, T_f=endset temperature

Explosion delay measurement

Explosion delays (D_E) at various high temperatures were measured for the complexes and the values are summarized in Table 3. The measurements were fitted [18–20]

$$D_E = A\exp(E^*/RT) \qquad (4)$$

where E^* is the activation energy for thermal explosion. Equation (4) in its logarithmic form, is used to determine E^* from the slope of a plot of $\ln D_E$ *vs.* T^{-1}. Plots of $\ln D_E$ vs. T^{-1} for these BPMP complexes are presented in Fig. 6 whilst calculated E^* are reported in Table 3.

Table 3 Explosion delay (D_E), activation energy for thermal explosion (E^*) and correlation coefficient (r) for BPMP complexes

Complex	D_E (s) at temperature/°C					E^*/kJ mol^{-1}	r
	300	350	400	450	500		
[Cr(pn)₂](ClO₄)₂	118.3	102.5	56.6	24.4	18.9	33.9	0.9997
[Mn(pn)₂](ClO₄)₂	117.0	99.9	54.8	22.3	18.5	32.0	0.9990
[Ni(pn)₂](ClO₄)₂	113.5	98.2	49.0	20.3	17.0	30.3	0.9998
[Cu(pn)₂](ClO₄)₂	110.0	92.8	46.4	19.1	15.5	29.7	0.9999
[Zn(pn)₂](ClO₄)₂	115.7	98.7	51.9	21.0	17.7	31.5	0.9989
[Cu(pn)₂](ClO₄)₂*	–	99.4	56.3	23.0	16.8	31.7	0.9995

*sample's mass≈10 mg

Discussion

It is clear from the analytical data given in Table 1 that estimated values of percentage mass of each element are in good agreement to those of calculated and thus confirming the formation of these complexes. In addition, the characteristic absorption frequencies of different groups in the complexes match well with those reported in the standard texts [21, 22]. All these complexes are anhydrous and metal:ligand ratio is found to be 1:2.

TG-DTA curves (Fig. 1) and data (Table 1) indicate that all the present complexes decompose in single step. The fast decomposition is attributable to a chain type explosive reaction due to simultaneous presence of oxidizing (ClO₄) and reducing (*pn*) group in the same complex molecule. It seems that an intramolecular solid phase redox reaction occurring between *pn* and ClO₄, is responsible for rapid decomposition. The formation of respective metal oxide as product of decomposition was confirmed by its colour, insolubility and negative test for Cl⁻. These observations are similar to those reported for thermal decomposition of some amine complexes of copper(II) nitrate [23] and nickel(II) nitrate [24, 25].

Changing of the atmosphere (from N₂ to air) does not cause any significant change in the mode of thermal decomposition. However, a lower value of endset temperature of decomposition (T_f) in air (Fig. 2) than that in N₂ is indicative of some what fast decomposition of the complexes in air and producing single exothermicity in DTA. Since, the thermal decomposition of such compounds involves complex processes, it may be speculated that the first step in the thermal decomposition may be dissociation of the compounds into pn and metal perchlorates, M(ClO₄)₂

$$[M(pn)_2](ClO_4)_2 \rightarrow 2pn + M(ClO_4)_2$$
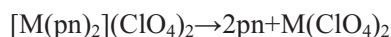
However, at normal pressure such a dissociation occurring in these perchlorates is difficult to detect by TG and DTA. The reason for this being the unstable nature of the metal perchlorates at higher temperatures,
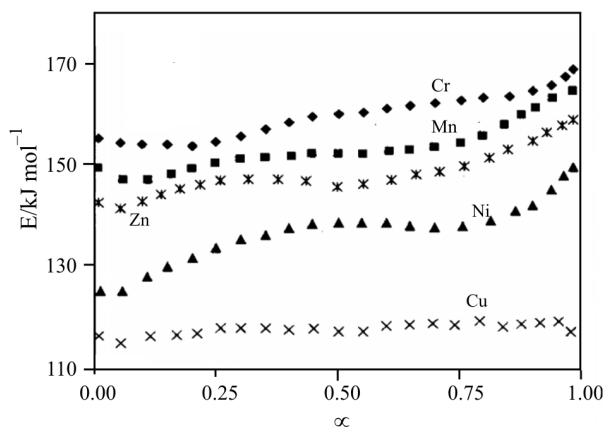
Fig. 5 Dependencies of activation energy on conversion for these complexes of the elements shown
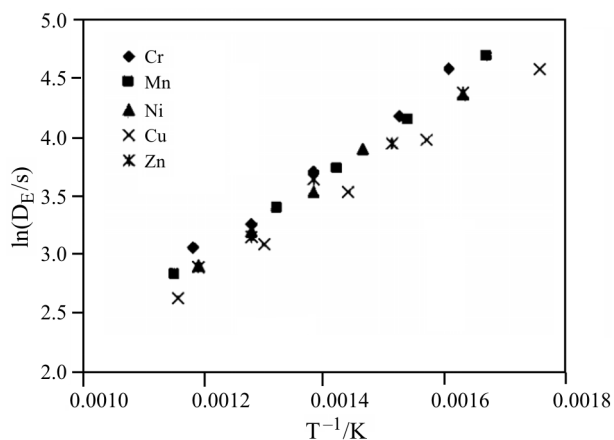
Fig. 6 Plot of ln(D_E) *vs.* 1/*T* for BPMP complexes of the elements shown

which would decompose instantaneously by exothermic reactions. The expected endothermic dissociation process may thus be completely overshadowed by exothermic process resulting in an overall exothermic effect. It was found appropriate to ascertain the contributions of endothermic dissociation and exothermic decomposition processes and thus DTA curves were recorded under various conditions with a constant sample mass. As the nature of the DTA curves were found
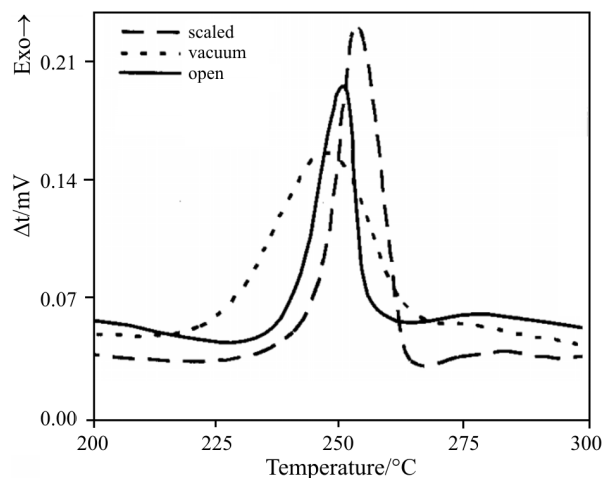
Fig. 7 DTA curves of Cu complex in various conditions

to be similar for all complexes, that of Cu is presented in Fig. 7 as representative. The reduction in the exothermic peak intensity under vacuum than that in air may be due to predominance of dissociation over exothermic decomposition. Thus, it seems that removal of pn molecules precedes the exothermic decomposition reactions. An increase of exothermic peak intensity in sealed cups than that in open may be due to decomposition of the complex at early stage and an increasing contribution of decomposition of gaseous products in later stages. Similar is the case with other complexes. The thermal stability of these complexes, as indicated by TG, decreases in the order:

$$[Cr(pn)_2](ClO_4)_2 > [Mn(pn)_2](ClO_4)_2 > [Zn(pn)_2](ClO_4)_2 > [Ni(pn)_2](ClO_4)_2 > [Cu(pn)_2](ClO_4)_2$$
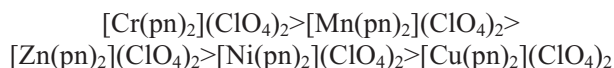
It was recorded that the exothermic peak temperature in DTA decreases in the same order.

The analysis of kinetics of isothermal TG using model fitting method results some uncertainty about mechanism because of composite nature of decomposition of these complexes. Out of various reaction models (Table 3), a 'best fit' model is selected on the basis of statistical parameter 'r', the model resulting $r \sim 1$ being the 'best fit'. As it was observed that there are many models having equal values of 'r' hence the selection of 'best fit' model becomes difficult. Also all these models result nearly equal values of E for a particular sample, irrespective of the equations used. Average values of 163.8, 155.4, 140.7, 118.9 and 148.3 kJ mol^{-1} have been obtained as E from different equations for isothermal decomposition of the complexes of Cr, Mn, Ni, Cu and Zn, respectively. It is difficult to assign this single value of activation energy to a particular process in complex decomposition reactions. A plot (Fig. 8) of all the values of E $vs.$ the respective ln$A$ obtained from different models indicates that these values fall in an almost straight line and hence show the existence of kinetic compensation effect.

The isoconversional method is known to permit estimation of apparent activation energy, independent of the model. In our case, we have adopted the isoconversional method suggested by Vyazovkin [26, 27]. This approach indicates that the decomposition of these complexes is not as simple as indicated by the model-fitting approach. The values of E for the complexes of Cr, Mn, Ni and Zn are lower initially (Fig. 5), but increase gradually when α increases from 0.6 to 1. The initial low value of E may be attributed to the removal of pn at early stage of decomposition which is partially governed by dissociation process while finally higher value may correspond to decomposition of anionic part (ClO_4^-) to respective metal oxides. For the complex of Cu, a fairly constant value of E may be due to highly explosive reaction and overlapping of different processes during heating. A period of induction (at lower α) and a period of acceleration (at higher α) controlled by nucleation and nuclei growth has been found to operate as general mechanism during thermal analysis.

In order to examine the response of the complexes in a condition of rapid heating, D_E was measured. The time required for thermal explosion at a particular temperature decreases in the order (Table 3)

$$[Cr(pn)_2](ClO_4)_2 > [Mn(pn)_2](ClO_4)_2 > [Zn(pn)_2](ClO_4)_2 > [Ni(pn)_2](ClO_4)_2 > [Cu(pn)_2](ClO_4)_2$$
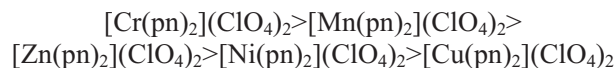
Thus, it should be noted that D_E data also show a trend similar to the thermal decomposition result. The relative thermal stability of the complexes are in the same order under the condition of rapid heating. Moreover, there appears to be a direct correlation between thermal decomposition and explosion. The values of E and E^* are in agreement with this order. The values of the decomposition temperature, E, time for
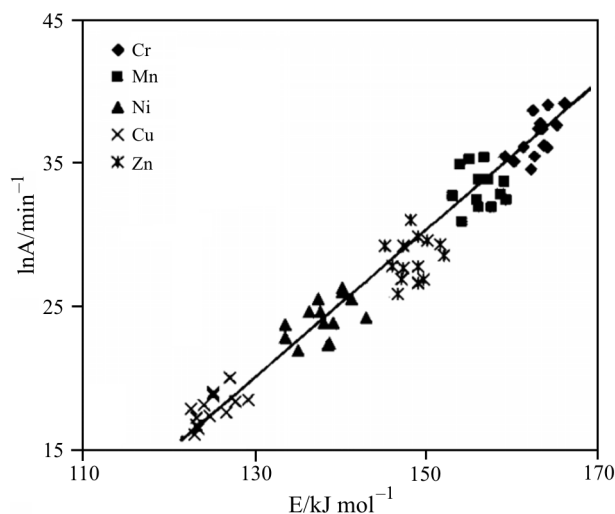

Fig. 8 The linear dependence of ln$A$ on E for all the complexes of the elements shown

explosion at a particular temperature and *E** are lowest for Cu and highest for that of the Cr complex. The ionic size of the central atom, their electron affinity, oxidation number etc., may be the contributing factor for this trend, but in absence of any firm data, these explanations remain conjectural. A decrease of sample mass (from 20 to 10 mg) causes an increase of time required for thermal explosion at a particular temperature (Table 3), which is indicative of self-heating of the samples. A similar variation of explosion time with the amount of the sample taken was studied with all the complexes.

Conclusions

The thermal studies carried out using TG-DTA (in N_2) and non-isothermal TG and DTA in air, provide an understanding of the nature of energetic complexes during thermal analysis. These complexes decompose in single step which are highly exothermic. The rate of decomposition is somewhat fast in air in contrast to nitrogen. A conventional model fitting approach fails to describe any change in the mechanism of the isothermal decomposition. The isoconversional method shows that the mechanism of thermal decomposition changes as the reaction proceeds. Measurements of D_E indicate that the mechanism of thermal explosion is the same for all these complexes.

Acknowledgements

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